

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 01-10-2012		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 2-Jul-2009 - 1-Jul-2012	
4. TITLE AND SUBTITLE Novel Polymers Containing Metal Ligands in the Side Chain Final Report				5a. CONTRACT NUMBER W911NF-09-1-0373	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 611102	
6. AUTHORS Gregory N. Tew				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Massachusetts - Amherst Office of Grants and Contracts University of Massachusetts Amherst Amherst, MA 01003 -				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 55975-CH.12	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This program aims to develop novel ferromagnetic materials and thin films from the directed self-assembly of novel block copolymers. Here, novel metal-ion containing monomers are polymerized into block copolymer architectures that organize the metal ions into nanostructured domains leading to ferromagnetic materials. In contrast, the unstructured homopolymer yields only small paramagnetic cobalt particles. The major differences between the two materials are highlighted in the figure here which shows the ferromagnetic sample with					
15. SUBJECT TERMS ROMP, metal-ligand, nanotechnology, block copolymers, self-assembly, magnetic. cobalt					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Gregory Tew
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 413-577-1612

Report Title

Novel Polymers Containing Metal Ligands in the Side Chain Final Report

ABSTRACT

This program aims to develop novel ferromagnetic materials and thin films from the directed self-assembly of novel block copolymers. Here, novel metal-ion containing monomers are polymerized into block copolymer architectures that organize the metal ions into nanostructured domains leading to ferromagnetic materials. In contrast, the unstructured homopolymer yields only small paramagnetic cobalt particles. The major differences between the two materials are highlighted in the figure here which shows the ferromagnetic sample with nanostructured cylinders beside the non-magnetic (paramagnetic) homopolymer with small, unstructured cobalt nanoparticles. Being able to build chemically rich monomers and place them into discrete locations within polymeric architectures will yield novel new materials. Funding this work will allow us to understand the fundamental connections between polymer chemistry, nanostructured self-assembly, and ferromagnetic response. It will lead to a new paradigm in materials synthesis in which the block copolymer is much more than a simple carrier of inorganic ions, which has been commonly exploited. Now the polymer chemistry and nanostructures are directly related to the final properties. More broadly, the opportunity to develop thin magnetic films with ultra-high density is of great promise. In addition, interest in magnetic materials for giant-magnetoresistance devices, magnetic sensors, and more are highly sought after.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
2012/10/01 1: 11	Hitesh D. Thaker, Raghavendra R. Maddikeri, Samuel P. Gido, Mark T. Tuominen, Gregory N. Tew, Yongping Zha. Nanostructured Block-Random Copolymers with Tunable Magnetic Properties, Journal of the American Chemical Society, (09 2012): 0. doi: 10.1021/ja305249b
2012/10/01 1: 10	Raghavendra R. Maddikeri, Semra Colak, Samuel P. Gido, Gregory N. Tew. Zwitterionic Polymersomes in an Ionic Liquid: Room Temperature TEM Characterization, Biomacromolecules, (10 2011): 0. doi: 10.1021/bm2010142
2012/10/01 1: 9	Jun Cui, Melissa A. Lackey, Ahmad E. Madkour, Erika M. Saffer, David M. Griffin, Surita R. Bhatia, Alfred J. Crosby, Gregory N. Tew. Synthetically Simple, Highly Resilient Hydrogels, Biomacromolecules, (03 2012): 0. doi: 10.1021/bm300015s
2012/10/01 1: 7	Ke Zhang, Gregory N. Tew. Cyclic Brush Polymers by Combining Ring-Expansion Metathesis Polymerization and the "Grafting from" Technique, ACS Macro Letters, (05 2012): 0. doi: 10.1021/mz2001675
2012/10/01 1: 6	Catherine N. Walker, Craig Versek, Mark Touminen, Gregory N. Tew. Tunable Networks from Thiolene Chemistry for Lithium Ion Conduction, ACS Macro Letters, (06 2012): 0. doi: 10.1021/mz300090m

TOTAL: 5

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

American Chemical Society SWRM, Austin, TX, Nov 2011

MIT, Dept. of Chemistry Seminar, Cambridge, MA, Nov 2011

Austrian-Slovenian Polymer Meeting, PCCL, Leoben, Austria, Jan 2012

University of Tennessee, Dept. of Chemistry Seminar, Knoxville, TN, Feb 2012

American Chemical Society Spring Meeting, San Diego, CA, Mar 2012

University of Iowa, Chemistry Seminar, Cedar Rapids, IA, May 2012

Polymer Chemistry 2012, Changchun, China, Jun 2012

IUPAC World Polymer Congress, Blacksburg, VA, Jun 2012

Number of Presentations: 8.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received

Paper

2012/03/04 2	4	Zoha M. AL-Badri, Raghavendra R. Maddikeri, Yongping Zha, Hitesh D. Thaker, Priyanka Dobriyal, Raja Shunmugam, Thomas P. Russell, Gregory N. Tew. Room temperature magnetic materials from nanostructured diblock copolymers, Nature Communications (09 2011)
2012/03/04 2	3	Ke Zhang, Melissa A. Lackey, Ying Wu, Gregory N. Tew. Universal Cyclic Polymer Templates, Journal of the American Chemical Society (05 2011)
2012/03/04 2	2	Jun Cui, Ke Zhang, Melissa Lackey, Gregory N. Tew. Hydrogels Based on Living Ring-Opening Metathesis Polymerization, Macromolecules (12 2010)
2012/03/04 2	1	Raja Shunmugam, Gregory J. Gabriel, Khaled A. Aamer, Gregory N. Tew. Metal-Ligand-Containing Polymers: Terpyridine as the Supramolecular Unit, Macromolecular Rapid Communications (05 2010)

TOTAL: 4

Number of Manuscripts:

Books

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Jun Cui	0.50	
Yongping Zha	0.50	
Cathy Walker	0.50	
Melissa Lackey	0.50	
FTE Equivalent:	2.00	
Total Number:	4	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ke Zhang	0.20
FTE Equivalent:	0.20
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Jun Cui

Yongping Zha

Total Number:

2

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attached report.

Technology Transfer

Nanostructured magnetic materials are important for many advanced materials; hence new methods for their fabrication are critical. However, coupling self-assembly to the generation of magnetic materials in a simple, straight-forward manner has remained elusive. Although several approaches have been considered, most have multiple processing steps, thus diminishing their use of self-assembly to influence magnetic properties. We show novel block copolymers that are pre-programmed with the necessary chemical information to microphase separate and deliver room temperature ferromagnetic properties following a simple heat treatment. The importance of the nanostructured elements is demonstrated by comparison with the parent homopolymer which yields only paramagnetic materials, even though it is chemically identical and has a higher loading of the magnetic precursor.

We recently showed that the block copolymers (BCPs) produced room temperature ferromagnetic materials (RTFMs) due to its nanoscopic ordering and the cylindrical phase yielded the highest coercivity. This was expanded to a series of metal-containing block-random copolymers composed of an alkyl-functionalized homo block (C_{16}) and a random block of cobalt complex- (Co) and ferrocene-functionalized (Fe) units was synthesized via ring-opening metathesis polymerization (ROMP). DC magnetic measurements, including magnetization versus field, zero-field-cooled and field cooled, as well as AC susceptibility measurements, showed that the magnetic properties of the nanostructured BCPs could be easily tuned by diluting the cobalt density with Fe units in the cylindrical domains. Decreasing the cobalt density weakened the dipolar interactions of the cobalt nanoparticles, leading to the transition from a room temperature ferromagnetic to a superparamagnetic material. These results confirmed that dipolar interactions of the cobalt nanoparticles within the phase-separated domains were responsible for the RTF properties of the nanostructured BCPs.

Monomer Synthesis. The same strained tricyclic monomer structure was used to provide similar polymerization rates and excellent initiation between blocks (Figure S1). The alkyl-functionalized monomer **2**¹⁴ and the Co monomer **4**³² were synthesized according to established procedures. Treatment of ferrocenemethanol with compound **1** afforded the Fe monomer **5** via Mitsunobu coupling (see Supporting Information for experimental details). The alkyl chain length of monomer **2** influences the microphase separation of the resulting BCPs, and a length of 16 (C_{16}) was chosen based on previous studies in which it exhibited the most well-defined microdomains.¹⁴ Block-random copolymers, **Poly1** - **Poly7**, with a C_{16} homo block and a Co-*r*-Fe block were synthesized by the stepwise polymerization of each block, as shown in Figure 1. First, the C_{16} homopolymer was prepared from monomer **2** by ROMP using the third generation Grubbs' catalyst (G3). When monomer **2** was completely consumed after 6 min, a mixture of monomers **4** and **5** was added to generate the block-random copolymers. The whole polymerization process required less than 15 min, and the monomer conversions for all of the polymers were ~99%, highlighting the efficiency of ROMP.

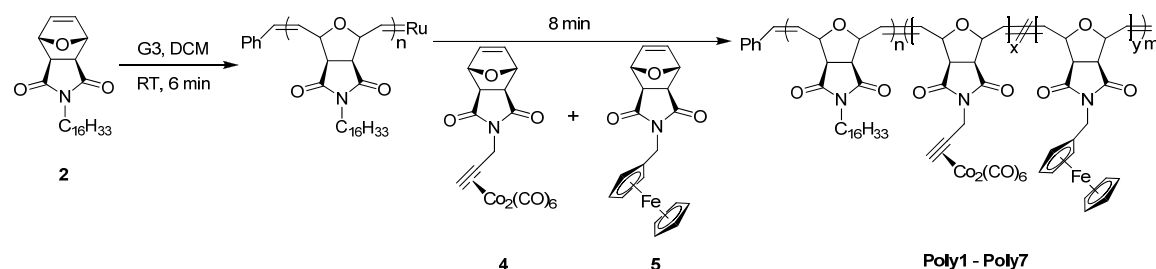


Figure 1. Synthesis of block-random copolymers **Poly1 - Poly7**.

To study the effect of the cobalt density in the cylindrical domains on the magnetic properties of the nanostructured BCP materials, a series of seven different block-random copolymers were synthesized. The composition details are listed in Table 1. All of the copolymers had similar molecular weights (MW) and narrow polydispersity indices (PDI). The molar ratio of the Co units (**4**) to the Fe units (**5**) in the Co-*r*-Fe block was varied from 80 : 20 to 20 : 80. Meanwhile, the volume fraction of the Co-*r*-Fe block was kept constant (0.23 ± 0.01) to ensure the same phase-separated morphology.

Table 1. Molecular characteristics of block-random copolymers **Poly1 - Poly7**

polymer	M_n^a (kDa)	M_w^a (kDa)	PDI ^a	4 : 5 (feed ratio)	x : y^b
Poly1	82	89	1.09	80 : 20	76 : 24
Poly2	89	96	1.08	70 : 30	66 : 34
Poly3	85	92	1.08	60 : 40	54 : 46
Poly4	83	89	1.07	50 : 50	39 : 61
Poly5	90	95	1.06	40 : 60	32 : 68
Poly6	94	99	1.05	30 : 70	23 : 77
Poly7	100	107	1.07	20 : 80	13 : 87

^a Determined by gel permeation chromatography (GPC) in THF using refractive index (RI) detector, relative to polystyrene standards. ^b Molar ratio of the Co units (x) to the Fe units (y) in the random block calculated from ¹H NMR integration. The deviation from the feed ratio is likely due to error in the NMR integration, as the characteristic peak used for monomer **5** is close to peaks at 4.62-4.32 ppm, which are attributed to the protons from the oxanorbornene backbone and the methylene group in the Fe units (Figure S2).

The diblock architecture of the resulting copolymers was confirmed by gel permeation chromatography (GPC). Figure 2 shows representative GPC curves for the first C₁₆ block and the final C₁₆-*b*-(Co-*r*-Fe) diblock copolymer (**Poly5**). A monomodal and narrow molecular weight distribution was preserved throughout. Only the cylindrical morphology was studied here, with a molar ratio of the C₁₆ homo block to the Co-*r*-Fe block of 70 : 30, so the final diblock (red curve) is never completely shifted to higher molecular weight compared to the first block (blue curve). There is no evidence of remaining C₁₆ homopolymer in the narrow monomodal curve for the final diblock, indicating efficient chain extension in the living polymerization.

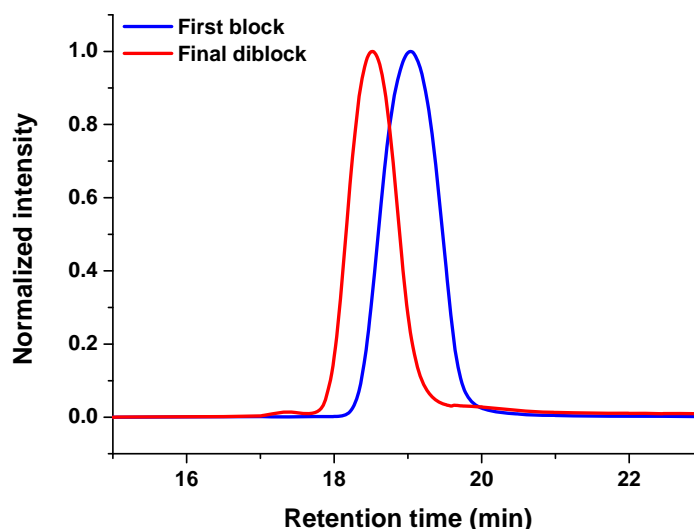


Figure 2. Representative gel permeation chromatography (GPC) curves for the first block composed of the C_{16} homopolymer (blue) and the final C_{16} -*b*-(Co-*r*-Fe) diblock copolymer (**Poly5**) (red).

The random copolymerization kinetics of the second Co-*r*-Fe block were investigated by ^1H NMR spectroscopy. Figure 3A shows the conversion as a function of time for the copolymerization of the Co monomer **4** (blue) and the Fe monomer **5** (red) for **Poly4** (feed ratio of **4** to **5** = 50/50). The conversions of the two monomers were almost identical at each time point, and both reached nearly 100% after 7 minutes. A living polymerization conducted isothermally is expected to be a first-order reaction,³³ and this should hold true for a random (gradient-free) copolymerization, as the relative monomer composition does not change with time.^{31,34} Figure 3B shows the first-order time-conversion plots of monomer **4** (blue), monomer **5** (red), and the sum of **4** and **5** (black). The $[\text{M}]_0/[\text{M}]$ values ($[\text{M}]$ denotes the monomer concentration) were obtained from the ordinate of Figure 3A. All three plots are linear, consistent with a polymerization that follows first-order kinetics with respect to the monomer. The monomer reactivity ratios, r_1 and r_2 , for the living random copolymerization of monomers **4** and **5** were determined by the Fineman-Ross method³⁵: $r_1 = 0.89$, $r_2 = 1.67$ (M_1 = monomer **4**, M_2 = monomer **5**). Although the r_1 and r_2 values calculated by this method should be treated with caution due to the steady-state assumption,³⁶ they indicate that the distribution of monomers **4** and **5** in the Co-*r*-Fe block is close to truly random.

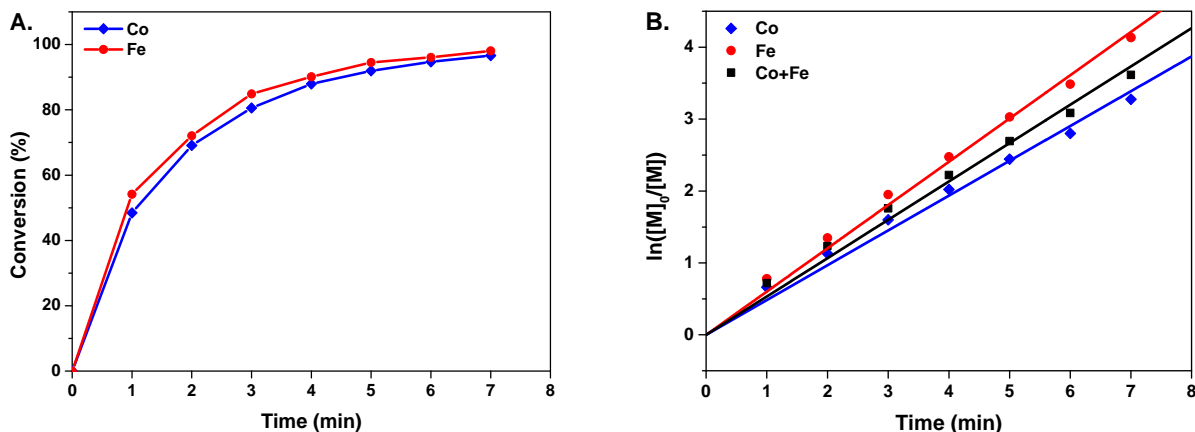


Figure 3. (A) Conversion of the cobalt complex-functionalized (Co) monomer **4** (blue) and the ferrocene-functionalized (Fe) monomer **5** (red) as a function of time for the random copolymerization of monomers **4** and **5**. (B) Linear fits of the first-order time-conversion relation of the Co monomer **4** (blue), Fe monomer **5** (red), and the sum of **4** and **5** (black). All the R^2 values for the linear fits are around 0.98. $[M]$ denotes the monomer concentration.

***M-H* measurement.** If the RTF behavior of the previously reported nanostructured BCP materials¹⁴ was due to the enhanced dipolar interactions between the cobalt nanoparticles under nanoconfinement, decreasing the Co unit percentage should dilute the density of the cobalt nanoparticles in the domains and weaken the dipolar interactions between them, leading to lower coercivity values.^{22,40} To investigate the effect of the cobalt density on the magnetic properties of the nanostructured BCPs, the magnetization as a function of the applied field (*M-H*) was measured at room temperature by a superconducting quantum interference device (SQUID) for all of the thermally treated block-random copolymers. The saturation magnetization values decreased with decreasing Co unit percentage in the Co-*r*-Fe block (i.e. decreasing cobalt density in the cylindrical domains). The coercivity values at room temperature (in Oe) were obtained from the x-intercepts of the hysteresis loops and are plotted as a function of the Co unit percentage in the Co-*r*-Fe block in Figure 4. The C₁₆-*b*-Co (100% Co units) and C₁₆-*b*-Fe (0% Co units) diblock copolymers (with cylindrical morphologies) were also synthesized and characterized (see Supporting Information for experimental details), and the results are included in Figure 4. As the cobalt density in the cylindrical domains decreased, the coercivity of the nanostructured BCP materials decreased from greater than 250 Oe to almost zero, consistent with our hypothesis.

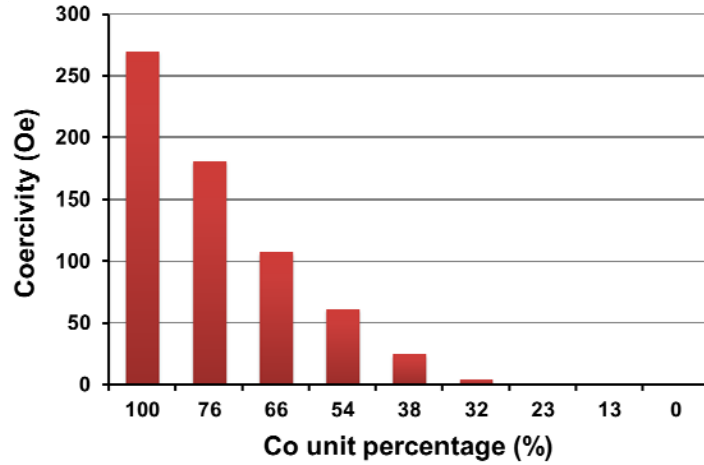


Figure 4. Impact of decreasing the Co unit percentage in the cylindrical domains on the coercivity of the nanostructured block copolymer (BCP) materials.

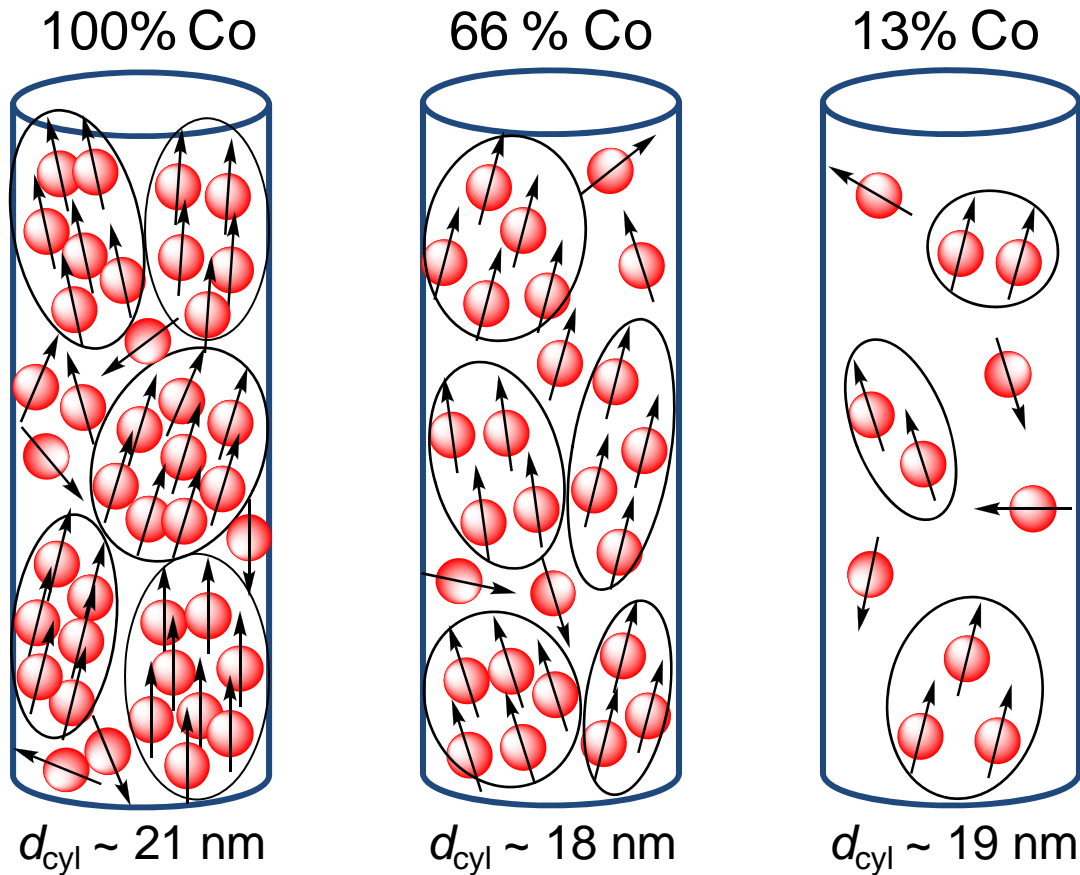


Figure 5. Schematic illustrating the decreased dipolar interactions between cobalt nanoparticles with decreasing cobalt density in the cylindrical domains. By controlling the number of cobalt units in the block copolymer, the density of cobalt atoms in the nano-cylinders is controlled. As the density decreases, the number of cobalt nanoparticles is decreased. This results in a larger average spacing between particles since the cylinder diameter is held constant. By increasing the

average spacing between particles, the dipolar interactions between cobalt nanoparticles (represented by the ovals) become weaker,²² leading to lower magnetic reversal temperatures.